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William Mairs Earnest

Union College - Schenectady, NY

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ELECTRODEPOSITION WITH GRADED CATHODE POTENTIAL

by

William Mairs Ernest

A thesis presented to the Department of Chemistry of
Union College in partial fulfillment of the requirements
for the degree of Bachelor of Science in Chemistry.

By William M. Ernest

Approved by Galen W. Ewing

Date 5/24/52

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Introduction

In a constant current electrolysis, which is the usual method of determining a substance quantitatively by electro-deposition, a single metal, in solution, is plated out on the cathode of the electrolysis cell. The current is maintained fairly constant by adjustment of the potential, and except for this adjustment, little attention is paid to the potential applied to the cell. This method may be used if there is only one metal in solution, or it may actually be used to separate two metals if one lies above and the other below hydrogen in the electromotive series. In this case, hydrogen is evolved at the cathode after the deposition of the first metal, and hydrogen will continue to be liberated as long as the pH of the solution is not too high. A good example is the determination of copper in a sulfuric acid solution containing zinc.

If, however, two metals lie close together in the electromotive series, their separation and determination using constant current electrolysis will prove impossible, since the two metals will come out together, or the second metal will start to plate out before the first is completely removed from the solution.

This problem of separating metals by electrolysis may be solved by another method called "Graded Cathode Potential Electrodeposition." In the case of the two metals, one above and the other below hydrogen in the electromotive series, the hydrogen being displaced acted as a control upon the cathode potential, keeping it at a certain value, which was the deposition potential of hydrogen. In graded cathode potential work, the same principle

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is used; a predetermined potential is chosen and the potential of the cathode is not allowed to fall below this value, preventing other metals from plating out.

Historical

The first reported electrolysis took place in 1800 when Nicholson and Carlisle discovered the decomposition of water by an electric current. By 1834, Faraday had discovered his important law governing the quantity of electricity and amounts of various metals involved in an electrodeposition. No attempts to cause a quantitative deposition were made, other than Faraday's work, until 1864, when W. Gibbs reported quantitative deposition of copper from solution. In 1876, Wrightson called attention to the fact that the accuracy of copper determinations was affected by the presence of "certain metals."

Graded cathode potential was first suggested in 1883 by Kiliani, and his work was later justified and elaborated by Freudenberg, who reported separation of several metals by controlling the potential between the electrodes. However, the method was not generally known or used until H. J. S. Sand (18), in 1906, developed a special technique for the measurement of the cathode potential relative to the solution using an auxiliary electrode. The method was much better than the earlier attempts, being independent of the cathode polarization and almost independent of the resistance of the solution.

Although Sand's method proved to be quite accurate, it did not come into general use as a means of analysis, probably due

to the tediousness of the procedure involved in the separations. Constant attention was required from an operator during the process. Sand, using currents as high as ten amperes, was able to keep the time of the run fairly short, but rapid fluctuations occur in the voltage at this current, and this was probably one of his main sources of error.

No new developments were made in this procedure until 1942 when Hickling (7) developed a completely automatic, electronic control device which governs the cathode potential during the entire course of an electrolysis and allows complete freedom of the operator. A slightly different type of control was developed by Caldwell, Parker, and Diehl (3), employing an electronic amplifier with a motor driven variable transformer to affect changes in current in the rectifier circuit which produces the electrolyzing currents.

A similar apparatus has been developed by Lingene (13) in which a motor-driven rheostat in the electrolyzing circuit is used to control the current. Still other apparatuses have been described by Thomas and Nook (20), and Foster (6).

The control set used in the present work was built by Carl Hirt (8) in 1951 and employs the Hickling circuit with the substitution of American Vacuum tubes. The main purpose of the present work was to investigate the worth of the set built by Hirt and to work out a scheme of analysis using the apparatus, so that it could be employed in the laboratories at Union College.

Theory

The total potential applied to an electrolysis cell in order to cause electrodeposition is a combination of several potentials:

$$V = (E_c + \omega_c) - (E_a + \omega_a) + IR$$

where E_c is the reversible half cell potential between the cathode and the solution; ω_c is the cathode polarization (overvoltage); E_a and ω_a are the corresponding terms for the anode; and IR is the potential drop between the cathode and the anode, R being the resistance of the solution between the cathode and the anode, and I , the current through the solution.

During most electrolysis reactions, oxygen is liberated at the anode, and since with conditions governing this reaction remain essentially constant, the term E_a is practically constant. The term ω_a is dependent upon the current density, but nevertheless, the sum $(E_a + \omega_a)$ may be considered to be about constant. All the rest of the terms vary during the course of the electrolysis.

The deposition at the cathode is determined by the term $(E_c + \omega_c)$. The values of E_c for metals follow the order of the electromotive series. The values of E^0 given in the series are for depositions from solutions in which the activity of the ions in solution is unity (1 gram ion per 1000 grams of solution), whereas during a deposition the activity of the metal ions will vary from an unknown starting activity a to a final activity of 10^{-6} molal or less depending on the accuracy of the determination. The actual value of E_c in a deposition at any concentration is given by the Nernst equation:

$$E_c = E^{\circ} + \frac{2.303RT}{nF} \log (a_{M^{+2}})$$

where R is the gas constant, T is the absolute temperature, F is the number of coulombs in one Faraday, n is the number of electrons involved in the reduction of the ion, and $a_{M^{+2}}$ is the activity of the metal ion in solution. At 25°C, the equation reduces to:

$$E_c = E^{\circ} + \frac{0.0591}{n} \log (a_{M^{+2}})$$

The chemical polarization at the cathode, ω_c , cannot be determined by an formula. It is only known that when a current is flowing, the cathode potential does not equal the equilibrium potential calculated by the Nernst equation, and the degree of departure from this value is dependent upon the size of the current flowing. With increasing current, the cathode potential is made more negative, or in other words, the effect is that of a decrease in the activity of the metal ions. This would suggest a depletion of the metal ions in the layer immediately surrounding the cathode, and this is probably one of the causes. However other factors undoubtedly enter into the picture, since rapid stirring should tend to eliminate this term at moderate current densities. Also if the electrode reaction is slow an additional potential or driving force may be required to carry on the reaction at the speed necessary for large currents.

We may sum up the foregoing by saying that if a solution is being electrolysed with appreciable current, the potential required is greater than the reversible electrode potentials due to irreversible changes taking place:

$$E_{\text{electrolysis}} = E_{\text{o(rev.)}} + E_{\text{irrev.}}$$

Since we are interested, mainly, in the reaction occurring at the cathode and since this is determined by the cathode potential, we must have a means of isolating and following this term during the electrolysis. This is where the use of Sand's method enters.

Consider the deposition of copper ions from solution onto platinum electrodes. As soon as some copper is plated out, the copper plated platinum electrode acts toward the solution like a copper electrode and this will have a half cell potential relative to the solution of its ions, the magnitude depending on the concentration of the ions. This half cell potential is the reverse of the electrolysis potential calculated earlier, and should be numerically equal to it.

Now, if we insert a standard, reference half cell, such as the normal calomel electrode, into the solution, we have a complete cell between the cathode and the reference electrode, and the potential of this cell can be measured. Since the reference cell is reversible only when a minute current is being drawn, the potential must be measured with a potentiometer or a vacuum tube voltmeter. The potential measured is the difference between the single electrode potentials of the half cell and the cathode:

$$E_{\text{CATH-REF.ELECT.}} = E_{\text{REF.ELECT.}} - (E_c + \omega_c)$$

and since we know the potential of the reference electrode, it is a simple matter to refer the cathode potential to the hydrogen scale.

If we plot the cathode potential (E_c) as ordinates against decreasing concentrations of metal ions as abscissas, we obtain the curves shown in figure I. Each metal ion will have a similar

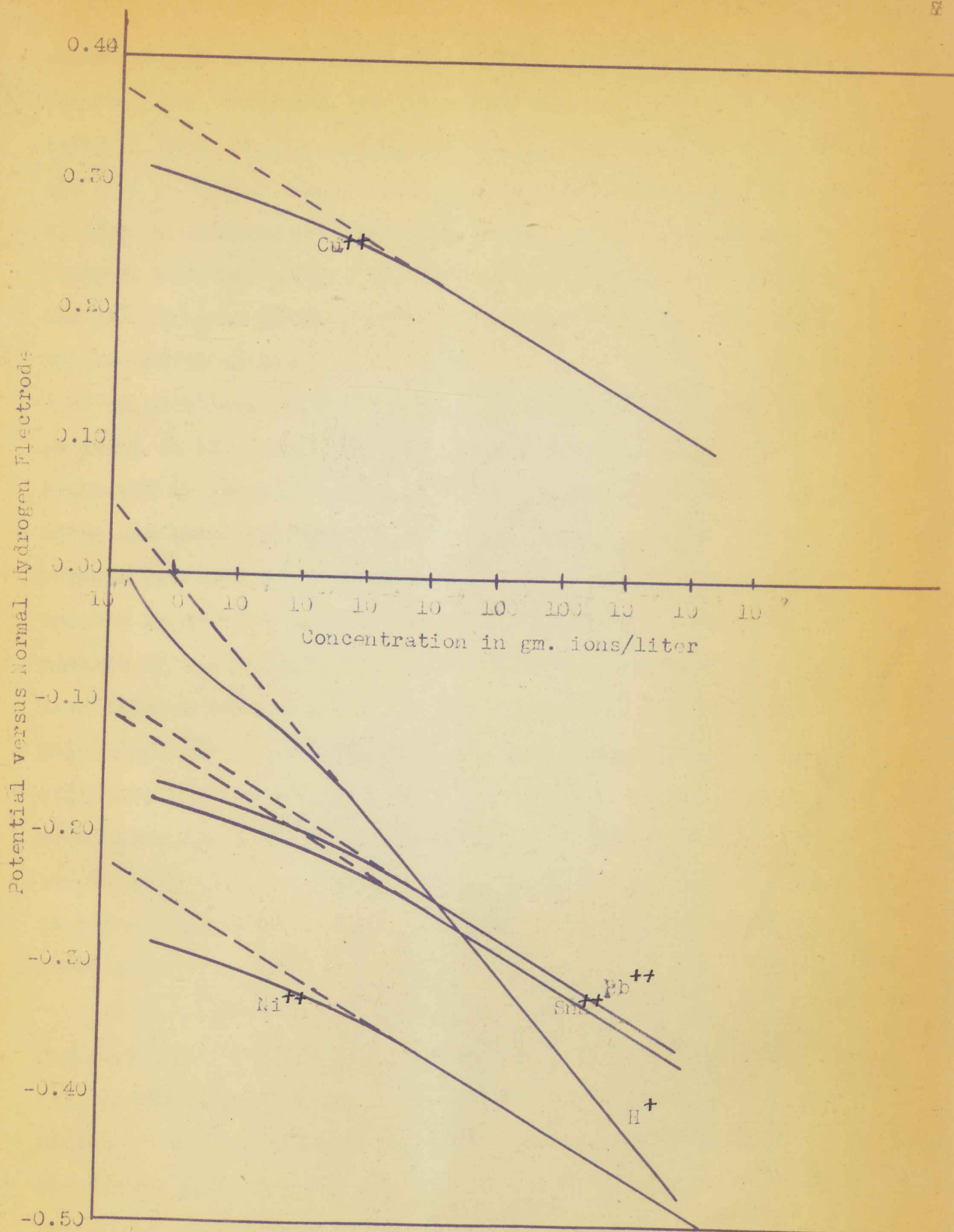


Figure I. Deposition potentials of several ions
(redrawn from Ewing ()).

curve, except for the slope, which is determined by the value of n . Thus the monovalent metals have a greater slope than the divalent metals. The low values on the first part of the curve are due to overvoltage effects and also to decreased activities of ions in the concentrated solutions. If the potentials were plotted directly against the activities instead of molarities, the curves would be straight all the way to the axis as shown by the dotted lines.

As an illustration, consider the copper and tin potentials as shown on the graph. Copper and tin cannot ordinarily be separated by constant current electrolysis, even though they lie above and below hydrogen on the electromotive series. This is because hydrogen has a rather high overvoltage on copper (21), and tin is reduced before hydrogen. However, if some exterior control is applied which will not allow the cathode potential to drop below a certain value for copper, say the potential at 10^{-6} molal concentration of copper ions, then a separation can be effected, since, no matter how long the cell remains in this condition, the potential will not drop far enough to cause deposition of tin. To control the cathode potential, the current is reduced gradually, until finally it reaches a value almost at zero, called the residual current \times .

This, essentially was Sand's original method. A rheostat was placed in the electrolyzing circuit and the cathode-reference cell potential followed with a potentiometer. When this potential reached a certain value, the current was reduced with the rheostat, and as the metal ion being deposited was depleted in the solution,

continual adjustments were made on the current to maintain the measured potential at the determined limiting value, until finally only residual current was flowing and the deposition was complete.

In the apparatus used in the present work, (see figure II), the electrolyzing current passes through five, type 1625 power tubes. The grid bias on the tubes is controlled by the potential drop across the 68J7 tube, which is in turn controlled by the thyatron circuit. This tube will pass no current when a negative bias is applied to its grid. This negative bias is supplied by a potentiometer, P, which will give any voltage from 0 to 3 volts.

If the potentiometer is set at the limiting potential for a given electrolysis, then it will control the thyatron until the cathode-reference electrode potential reaches the limiting potential, at which point the grid bias will be nearly zero and the thyatron will "fire" or start to pass current. The more the cathode-reference electrode potential increases, the more current will flow through the thyatron. As soon as the thyatron starts to pass current, it overcomes a negative bias on the 68J7 tube, which in turn starts to allow current to flow, increasing the bias on the 1625 tubes, and so decreasing the amount of current through these tubes. The whole process from the moment the 884 tube fires is practically instantaneous, and the effect on the electrolyzing current is immediate.

Thus, once the electrolyzing current has been applied and the potentiometer is set at its limiting potential, no attention is necessary by the operator until the deposition is complete.

Hirt used a reference electrode which consisted of a platinum foil electrode covered with lead dioxide and immersed in a one normal solution of sulfuric acid. The electrode reaction is ():

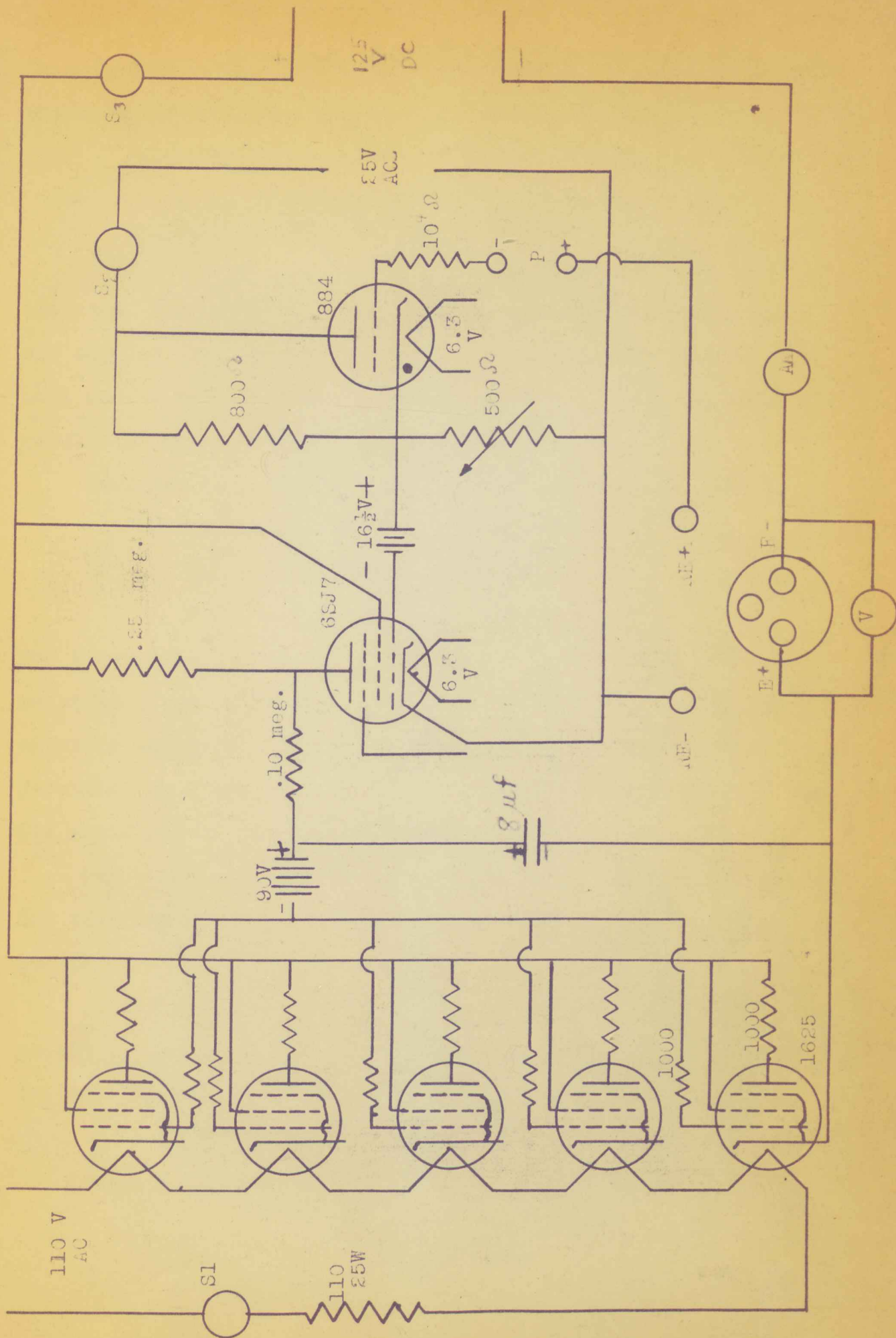
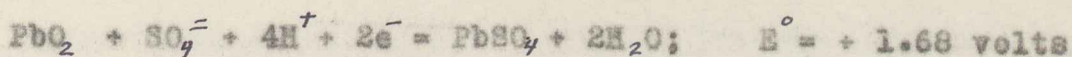


Figure II - Circuit Diagram

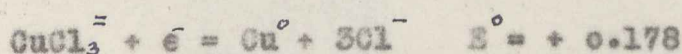
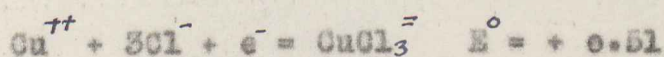
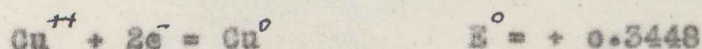


The value of E° is for exactly one normal acid.

Chloride Complex Theory

Some work was done in chloride solution, and this phase of the work involves some theory not already covered, especially for copper. The theory of deposition in chloride solution has been worked out in detail by Diehl and Broune (5), and only the results of their investigations will be used here.

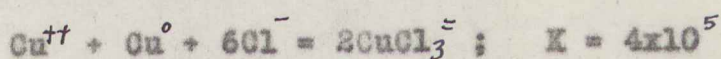
Consider the following reduction reactions for copper:



The first reaction is the reduction of cupric ion in sulfate solution. The second and third are the reductions involved in chloride solution. The large deviation of the final reduction potential in chloride solution from that in sulfate is due to the stability of the chloridocuprous ion.

The reaction in chloride solution takes place in two steps, and the first step takes place completely before the second step starts.

At the anode, the chloridocuprous ion is reoxidized to the cupric ion. The cupric ion in turn reacts with the copper deposited on the cathode and dissolves it:



The reaction is very rapid, as shown by the large value of K .

The suggestions of Diehl and Brouns to overcome this anodic reoxidation of copper are: "(1) the use of a reducing agent which will be oxidized in preference to the chloridocuprous ion; (2) increasing the initial cathode voltage to a value sufficient to instantly reduce to metallic copper more than half the chloridocuprous ions formed before the latter have been stirred away from the vicinity of the cathode; (3) isolation of the anode by means of a membrane or a porous cup; (4) reduction of the anode potential to a value which will not oxidize the chloridocuprous ion."

Experimental Work and Results

Since the apparatus had not been used or tested adequately, the first trials were made on a simple copper sulfate solution, containing some sulfuric acid. In the initial runs, the deposition was incomplete and occasionally the instrument did not even shut off.

This trouble was partially due to a faulty reference electrode and partially due to fluctuations in the line voltage which powered the set. It is very difficult to electroplate lead dioxide smoothly on platinum so that it will adhere well. Best results are obtained if a very small current is used and the electrolysis is allowed to take place for a half hour or more.

Fluctuations caused the line voltage to run as low as 100 volts in the late afternoons. These fluctuations have proved a nuisance in general to the laboratories in the chemistry buildings. Once they were noted, the remedy was simple. A Sola saturated core, constant voltage transformer was placed between the line and the set. This transformer gave a constant voltage output of 115 volts for input values ranging from 95 to 120 volts. This had a very good effect on the operation of the set and it is recommended that the transformer be used in all further work.

Hirt describes the set as designed to deliver 300 milliamps maximum. It was noted at this point that the maximum attained under any conditions was 240 milliamps. A check of the circuit disclosed a wiring mistake on one of the 1625 tubes. When this was corrected, the maximum current was found to be 300 milliamps, as specified. From this point on, the apparatus was functioning exactly as it was intended.

If the operator is to be free from the set, he must be able

to leave it for periods of time. Yet he will want to know when one phase of a multiple operation is complete so that he may start the next phase. To make this possible, a signal light, consisting of a neon "glow" lamp was placed across the .25 megohm resistor in the circuit, so that when the thyatron fires, the lamp lights and the operator may tell from a distance that the operation is nearly finished.

With the transformer in use, consistent results were immediately obtained for a copper sulfate solution. The limiting values set on the potentiometer are the cathode-reference cell potentials, as previously noted. The reference electrode will vary slightly with time, decreasing as much as .05 volts from day to day. Therefore it was found necessary to check the potential of the electrode each day against a standard calomel electrode, using the same potentiometer employed in the set. When the reference cell potential is obtained, the cathode potential, in 10^{-6} molar solution of the ion to be removed, is calculated from the Nernst equation and this value is subtracted from the reference electrode potential to give the limiting potential.

10 ml. of the copper sulfate solution was pipetted into a tall form, Pyrex beaker, 5 ml. of H_2SO_4 were added, the solution was diluted to 150 ml. and the electrolysis begun. The values of copper from copper sulfate from three consecutive runs are as follows:

Gm. Copper Found

0.1958 Gm.

0.1968 Gm.

0.1962 Gm.

Ave. 0.1963 .0005 Gm.

This solution was not a standard, since the main idea was to obtain consistent results. Completeness of deposition was tested by adding NH_4OH to a small sample of solution, to see if any copper ammonia complex was formed.

The calculation for the limiting potential of Cu in sulfate is:

$$\begin{aligned}\text{Cu}^{++} + 2\text{e}^- &= \text{Cu}^0 & E &= + 0.3448 \text{ Volt} \\ E_c &= + .3448 + \frac{.0591}{2} \log(10^{-6}) \\ &= + .168 \text{ Volt}\end{aligned}$$

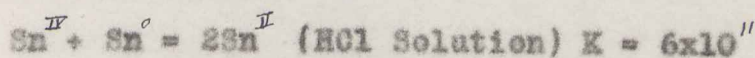
A slightly higher value must be set on the potentiometer, due to overvoltage effects, and the size of this excess value must be determined experimentally. If the residual current is low, the overvoltage is negligible.

Next it was decided to attempt a simple determination of tin to see if any difficulties were encountered, before proceeding with an actual separation. The most convenient tin salt is the chloride, but it was found that the tin would not plate out completely in chloride solution. Three runs were made, varying the acidity of the solution, but no consistent results were obtained, only about half of the tin plating out if at all. Hydroxylammonium chloride was added to prevent the deposition of chlorine on the anode. This is the method of Schoch and Brown (19).

A check of the literature showed that the potential for the chloride complex is different, appreciably, from that in sulfate. The sulfate value is $- 0.136$, whereas the chloride value is $- 0.19$ volts. This value for chloride was tried, in calculating a limiting potential, and a run was made on the tin chloride

solution. The deposition was still not complete. Three more runs were attempted, varying the acidity, but no improvement was seen. According to the theory of Schoch and Brown, in the absence of a reducing agent, chlorine is liberated at the anode, and this observation was verified, but Schoch and Brown state that the chlorine liberated is the cause of incomplete deposition on the cathode, the metal going into solution as fast as it comes out. Moreover, in the presence of a reducing agent, such as hydroxylammonium chloride, they report good results, the greatest error in 5 runs being 0.24%. The instructions of Schoch and Brown were followed as closely as possible, but accurate results were not obtained.

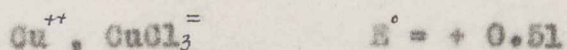
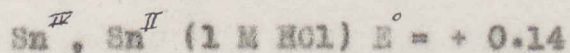
The theory of Diehl and Brouns, of anodic reoxidation of complex ions in solution, seemed more plausible. Diehl and Brouns worked out the theory in detail for copper, but estimated that equivalent reactions for tin and antimony should occur. In fact they report that:



and it appears that anodic reoxidation in tin chloride solution could affect the deposition as much as in copper chloride solution.

Diehl and Brouns developed four methods of preventing anodic reoxidation. The first, the use of a reducing agent which is more easily reduced than the chloridocuprous ion, is the most applicable in the present instance. The second, raising of the cathode potential, may also be applied but does not show any marked effect. The third, use of a porous cup or membrane, requires complex equipment which is awkward to use, and the

fourth, lowering of the anode potential by a change of the anode material, give poor results. Therefore, the following work was done attempting to make use of the first method. Stannous ion will work as a successful reducing agent in the case of the chloridocuprous ion. Potentials involved are:



The stannous ion will be oxidized in preference to the chloridocuprous ion and also, the stannic ion will be reduced again at the cathode to stannous ion, so as long as tin is present in solution, no anodic reoxidation of copper will take place. This was tried and found true. A simple copper chloride solution will not deposit any copper, or if any, not all the copper present. The addition of tin will cause good separation. Values of three runs are shown in table 2.

Table 2

<u>Gram Cu present</u>	<u>Gram Cu found</u>	<u>Error</u>
0.1963	0.1958	- 0.0005
0.1963	0.1970	+ 0.0007
0.1963	0.1968	+ 0.0005

DEPOSITION OF COPPER FROM A CHLORIDE SOLUTION CONTAINING TIN

However, ^{as} it was still impossible to obtain consistent results for the tin, it was decided to prepare some titanium III chloride solution, which would prevent anodic reoxidation of tin, if such was occuring.

Various synthetic methods were tried. TiO_2 was heated with carbon to 600°C and Cl_2 was passed over the mixture. Instead of a liquid product, TiCl_4 , a yellow crystalline solid appeared in the condenser. This solid dissolved readily in HCl , and when the solution was reduced with metallic zinc, the characteristic purple color of titanium III solutions appeared. However it was found impossible to get a solution concentrated enough for the present work, so the idea was abandoned, it now being too late in the term to order some titanous chloride from a commercial supply house.

Next the copper in an analyzed german silver was determined by dissolving the sample in HCl , adding stannous ion and electrolyzing. Two samples taken gave values in percent of 48.49% and 48.62%, a difference of only 0.13%. However, the mean value is nearly one percent below the specified value, 49.75%. This would indicate a systematic error, causing low results in all samples, so the apparatus was rechecked to see if any changes had occurred in circuit potential values during the course of the years work. No defects could be found, and the end of the term was approaching so it was necessary to forego further tests.

Summary

The set is apparently working as intended. Copper may be deposited quantitatively from sulfate solution using the apparatus and from chloride solution, if tin is present. Since tin prevents anodic reoxidation, titanous ion should do so.

If the apparatus could be redesigned so that it will pass more current, it would be more easily used.

Bibliography

- 1) Allen, M. J., Anal. Chem. 22, 804, (1950)
- 2) Ashley, S. E. Q., Anal. Chem. 24, 91, (1952)
- 3) Caldwell, C. W., Parker, R. O., and Diehl, H., Ind. Eng. Chem., Anal. Ed. 16, 532, (1944)
- 4) Chambers, F. W., J. Sci. Instruments, 27, 292, (1950)
- 5) Diehl, H., Electrochemical Analysis with Graded Cathode Potential, C. Frederick Smith Chemical Co., Columbus, Ohio, (1948)
- 6) Foster, D. C., J. Chem. Ed. 28, 626, (1951)
- 7) Hickling, Trans. Faraday Soc. 38, 27, (1942)
- 8) Hirt, C. A., Electrodeposition Apparatus Employing A Controlled Cathode Potential Undergraduate Theses, Union College Library, (1951)
- 9) Lamphere, R. W., Anal. Chem. 23, 258, (1951)
- 10) Lindsey, A. J., Analyst 73, 99, (1948)
- 11) Lingane, J. J., Ind. Eng. Chem. Anal. Ed. 17, 332, (1945)
- 12) Lingane, J. J., and Jones, S. L., Anal. Chem. 22, 1169, (1950)
- 13) Lingane, J. J., Anal. Chem. 21, 497, (1949)
- 14) Lingane, J. J., Ind. Eng. Chem., Anal. Ed. 16, 147, (1944)
- 15) Lingane, J. J., Swain, C. G., and Fields, M., J. Am. Chem. Soc., 65, 1348, (1943)
- 16) Lingane, J. J., and Jones, S. L., Anal. Chem., 23, 1798, (1951)
- 17) Pentthner, C. J., and Pompeo, D. J., Anal. Chem., 21, 178 (1949)
- 18) Sand, H. J. S., J. Chem. Soc., 91, 373, (1907)
- 19) Schoch, E. P., and Brown, D. J., J. Am. Chem. Soc., 38, 1660, (1916)
- 20) Thomas, E. B., and Hook, R. S., J. Chem. Ed., 27, 217 (1950)
- 21) Willard, Merritt, and Dean, Instrumental Methods of Analysis 2nd Ed. P236-262, D. Van Nostrand Co., Inc., New York (1951)